



# Occurrence and air–soil exchange of organochlorine pesticides and polychlorinated biphenyls at a CAWNET background site in central China: Implications for influencing factors and fate



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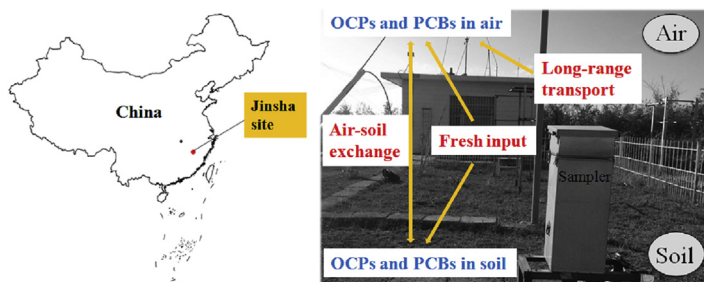
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## HIGHLIGHTS

- Air and soil samples were simultaneously collected at a central China background site.
- Concentrations of OCPs and PCBs in soil and air were lower or comparable with other remote/background sites.
- Soil was an important source for atmospheric *p,p'*-DDT, endosulfans, and chlordanes.
- Higher HCB concentrations in winter were attributed to the surrounding ongoing source.
- Atmospheric HCHs and PCBs were mainly influenced by long-range atmospheric transport.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Ambient air and soil samples were collected between March 2012 and March 2013 at Jinsha, a regional background site in central China, to measure the concentrations of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs). The average concentrations of total OCPs and total PCBs were  $191 \pm 107$  and  $39.4 \pm 27.1$   $\text{pg}/\text{m}^3$  in air (gaseous and particulate phase) and  $0.585 \pm 0.437$  and  $0.083 \pm 0.039$   $\text{ng}/\text{g}$  in soil, respectively. The higher concentrations of *p,p'*-dichlorodiphenyltrichloroethane (*p,p'*-DDT) and *p,p'*-DDT/*p,p'*-DDE ratios in the soil indicated recent *p,p'*-DDT input to the soil. A strong positive temperature dependence and average fugacity fraction value  $> 0.5$  were observed for *p,p'*-DDT, suggesting that volatilization of residual DDT in the soil was the main influencing factor on atmospheric *p,p'*-DDT. Highly average fugacity fractions ( $> 0.7$ ) of *trans*-chlordane (TC) and *cis*-chlordane (CC) and high TC/CC ratios both in the soil and atmosphere suggested fresh inputs. Higher gaseous concentrations of hexachlorobenzene (HCB) were observed in winter and negative temperature dependence was directly attributed to the surrounding ongoing source (e.g. fuel consuming activities), especially in winter. Overall, most targeted OCPs and PCBs were influenced by long-range transport, and fugacity fraction values indicated highly volatile compounds (e.g.  $\alpha$ -hexachlorocyclohexane ( $\alpha$ -HCH) and lower chlorinated PCBs) were volatilized and low volatility compounds (e.g. *p,p'*-DDE and higher

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chlorinated PCBs) were deposited at the air–soil interface. Knowing the source and sink of OCPs and PCBs can help to control their pollution in this area and provide a reference for other studies.

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## 1. Introduction

Persistent organic pollutants (POPs) are a class of organic chemicals that have high persistence in soil, water, sediments or biota and can be transported over long distances in the atmosphere or water (Wania and Mackay, 1996; Fu et al., 2003). Because of their semi-volatility, POPs may volatilize from soils into the atmosphere after application. The processes of volatilization and deposition cause the soil to be an important source or sink for the regional or global cycling of POPs in the atmosphere (Jones and Voogt, 1999; Meijer et al., 2003).

Organochlorine pesticides (OCPs), one of the best-known POPs, are a series of man-made chemicals that were widely produced and used in China as insecticides from 1950 to 1983 (Fu et al., 2003; Wong et al., 2005; Jin et al., 2010; Tasdemir et al., 2012). China has prohibited the production, usage, and circulation of Dichlorodiphenyltrichloroethanes (DDTs), hexachlorocyclohexanes (HCHs), chlordane and hexachlorobenzene (HCB) after signing the Stockholm Convention in May 2001. However, usage of DDT-containing dicofol, technical chlordane, lindane and endosulfan still continues in China, contributing to higher levels of OCPs pollution (Bidleman et al., 2002; Qiu et al., 2005; Wang et al., 2012a). Polychlorinated biphenyls (PCBs) are one of the target twelve POPs in the Stockholm Convention (Li et al., 2010). The production of PCBs in China was started in 1965, began to be restricted in 1974 and totally banned in the 1980s (Fu et al., 1997; Breivik et al., 2002). During the production period, about ten thousand tons of PCBs were produced as raw materials for the manufacture of transformers and power capacitors or as additives for paint. Transformer and power capacitor waste and the paint additives can lead to environmental pollution (Bi et al., 2002). Until recently, these compounds were still detected in the various environmental media (e.g. soil, atmosphere, etc.) in China (Wu et al., 2011; Cui et al., 2013; Yuan et al., 2014; Zhao et al., 2016).

Recently, the transport and fate of OCPs and PCBs in the environment have been largely influenced by the process of soil–air exchange with the secondary sources becoming increasingly influential (Bidleman and Leone, 2004; Valle et al., 2005). The exchange directions of the chemicals between the soil and air can be characterized by the equilibrium between the two phases (Harner et al., 2001). There are many studies focusing on the soil–air exchange of OCPs and PCBs over the world (Meijer et al., 2003; Tasdemir et al., 2012; Wang et al., 2012b). Wang et al. (2012b) founded that HCB and lower chlorinated PCBs in Tibet were largely from the re-volatilization of the soil, whereas there were net deposition of DDTs to the soil. Li et al. (2010) reported global fugacity fraction (ff) for PCBs and the ff values were quite low at background sites in China, indicating that the background sites will likely continue to be “sinks” for PCBs. Růžičková et al. (2008) assessed air–soil exchange of OCPs and PCBs across central and southern Europe, the results showed that soil in background sites were sink for higher chlorinated PCBs, DDT, and  $\gamma$ -HCH while they were tend to be source for most of the PCB congeners, as well as for  $\alpha$ -HCH.

Jinsha (JSH) is a regional background Chinese Meteorological Administration (CMA) Atmosphere Watch Network (CAWNET) site, which is located in a sparsely populated area in central China. To

date, studies of environmental contaminants in air and soil were limited at JSH. Lin et al. observed the background concentrations of reactive gases and illustrated the impact of long-range atmospheric transport (LRAT) at JSH (Lin et al., 2011). Zhang et al. investigated the chemical compositions and seasonal variations of fine particles at JSH, finding that the high levels of PM<sub>2.5</sub> in winter were most likely caused by the LRAT from the north of JSH and strong regional emissions (Zhang et al., 2014). Since different economic development levels and historical usage in different areas, observations of OCPs and PCBs were mostly concentrated in the highly-polluted southeast coastal areas. To our knowledge, no studies on the occurrence of OCPs and PCBs at JSH (central China) have been published. This study was conducted to 1) investigate the concentrations and seasonal variations of OCPs and PCBs in air and soil at JSH; 2) assess the key influencing factors on atmospheric concentrations according to the results of temperature dependence and air–soil exchange; and 3) identify the potential sources and fate of the regional contaminants.

## 2. Materials and methods

### 2.1. Sampling site and sample collection

JSH (29°38'N, 114°12'E, 750 m.a.s.l.) is a regional background CAWNET site situated at the junction of Hunan, Jiangxi and Hubei provinces and geographically close to the center of China (Fig. 1). It is one of CAWNET sites across China operated by the CMA to monitor the meteorological data and concentrations of contaminants in the environment. The JSH site is on an isolated mountain peak, and the surrounding area is naturally scattered grasslands and is sparsely populated. During the whole year sampling period, the average temperature was 16.3 °C, and the average relative humidity was 78.6%. The prevailing wind directions were NNW, NW, ESE and SE, with an average wind speed of 3.7 m/s.

Air samples were collected for 24 h approximately every 6 days from March 2012 to March 2013, using a modified Anderson-type Hi-Volume air sampler which was operated at a rate of 0.3 m<sup>3</sup>/min. Samples were also collected on days of very high pollution. A total of 64 samples were collected. Air particulates were collected on quartz fibre filters (QFFs) (Grade GF/A, 20.3 × 25.4 cm), and POPs in gaseous phase were collected by polyurethane foam (PUF) plug (length 8.0 cm, diameter 6.25 cm, density 0.035 g/cm<sup>3</sup>). The QFFs were baked in an oven at 450 °C for 4 h to remove organic contaminants before use. The PUF plugs were precleaned using an Accelerated Solvent Extraction (ASE) extractor with 2 extraction steps, each last for 15 min at 100 °C and 1500 psi, using a mixture (1:1, V/V) of acetone and dichloromethane (DCM). The samples were sealed in glass bottles and stored below –18 °C until analysis.

A total of 15 soil samples were collected approximately once a month around the air sampler (<10 m). About 1 kg of soil samples were taken from the top 5 cm of the soil after removal of the large stones and pieces of vegetation. After sieving through a 1.0 mm mesh to remove large particles and organic debris, the soil samples were sealed with aluminum foil and stored at 4 °C. About 30 g of soil samples were used to determine the contents of organic carbon, and 15 g were used for OCPs and PCBs analysis.

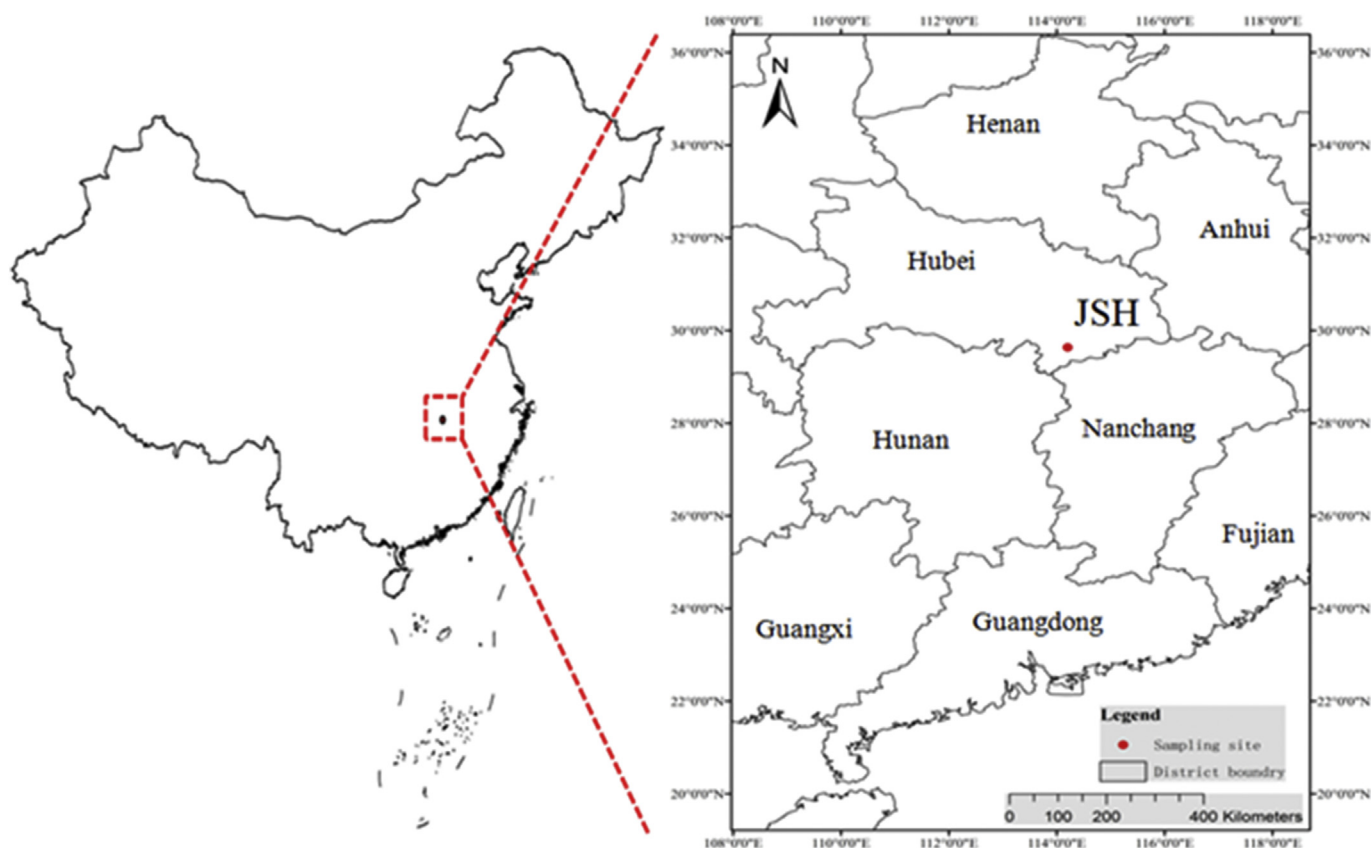


Fig. 1. Location of JSH sampling station in central China.

## 2.2. Extraction and analysis

Prior to extraction, 10 ng surrogate recovery standards (2, 4, 5, 6-tetrachloro *m*-xylene (TCmX), PCB 30 and PCB 198, PCB 209) were added to each of the samples. Activated copper granules were added to the collection flask to remove elemental sulfur. All the collected soils, PUF plug and QFFs were extracted separately with (1:1, v/v) DCM in hexane for 24 h in a soxhlet apparatus. The extracts were concentrated to a volume of 1 mL using a Rotary evaporator. The elute was cleaned up by 7 mm i.d. alumina/silica column including anhydrous sodium sulphate (1 cm), neutral silica gel (3 cm, 3% deactivated) and neutral alumina (3 cm, 3% deactivated). OCPs and PCBs were collected by eluting the column with a mixture of dichloromethane and hexane (1:1, v/v). The samples were reduced to 0.2 mL under a gentle stream of nitrogen and exchanged into 25  $\mu$ L of dodecane. Then 20 ng of pentachloronitrobenzene (PCNB) and PCB54 were added into each sample with 0.2 mL in bottles as internal standards for analyzing OCPs and PCBs.

32 PCBs (PCB 8, 28, 37, 44, 49, 52, 60, 66, 70, 74, 77, 82, 87, 99, 101, 105, 114, 118, 126, 128, 138, 153, 156, 158, 166, 169, 170, 179, 180, 183, 187, 189) and 15 OCP compounds ( $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH,  $\delta$ -HCH, *o,p'*- and *p,p'*-DDE, -DDD and -DDT, *trans*-chlordane (TC), *cis*-chlordane (CC),  $\alpha$ -endosulfan,  $\beta$ -endosulfan, HCB) as one injection were determined by an Agilent 7890/7000 GC-MS/MS with a capillary column (VARIAN, CP-Sil 8 CB, 50 m, 0.25 mm, 0.25  $\mu$ m). The mass spectrometer was operated with an EI source ( $-70$  eV) in multiple reaction monitoring (MRM) mode. The temperatures of the transfer line, injector interface and ion source were set at 280  $^{\circ}$ C, 250  $^{\circ}$ C and 230  $^{\circ}$ C, respectively. The GC oven temperature program was set at 80  $^{\circ}$ C for 0.5 min, then 20  $^{\circ}$ C/min to 160  $^{\circ}$ C, 4  $^{\circ}$ C/

min to 240  $^{\circ}$ C, and finally 10  $^{\circ}$ C/min to 295  $^{\circ}$ C, and hold for 10 min. For each analysis, 1  $\mu$ L of sample was injected in splitless mode. Helium was used as the carrier gas at the flow rate of 1 mL/min. Collision induced dissociation (CID) gas and quench gas in the collision cell were nitrogen and helium at the flow rates of 1.5 mL/min and 2.25 mL/min, respectively.

## 2.3. Quality assurance and quality control

Chemical standards were purchased from Accustandard Co. U.S. Laboratory. Lab blanks were pre-cleaned PUF plugs and filters. Field blanks were obtained by transporting and handling pre-cleaned PUF plugs and filters in the exactly same way as samples. Lab and field blanks were subject to the same storage and analytical procedures as samples, which constituted less than 10% of the total number of samples analyzed. Surrogate standards were added to all the samples to monitor procedural performance and matrix effects. The recoveries for TCmX, PCB 30 and PCB 198, PCB 209 in atmospheric samples were  $73.3 \pm 4.9\%$ ,  $72.5 \pm 5.3\%$ ,  $86.2 \pm 6.3\%$  and  $89.5 \pm 7.6\%$ , respectively, while those in soil samples were  $72 \pm 6.5\%$ ,  $80 \pm 8.3\%$ ,  $90 \pm 8.2\%$  and  $94 \pm 10.5\%$ , respectively. All the data were blank corrected using the mean of the field blanks. The final concentrations of OCPs and PCBs were not corrected by the recovery of surrogates. The method detection limits (MDL) were stemmed from the field blanks and quantified as the mean of the blanks plus 3 times the standard deviations of the blank concentrations. MDLs ranged from 0.02 to 0.5  $\text{pg}/\text{m}^3$  for air samples and 0.4–1  $\text{pg}/\text{g}$  for soil samples. A backup PUF plug was attached to the sampler to check the possible breakthrough of gaseous phase of OCPs and PCBs by analyzing the top and bottom PUF plugs separately and results showed that the breakthrough can be ignored.

### 3. Results and discussion

#### 3.1. Atmospheric concentrations of OCPs and PCBs

The concentrations both in the gaseous and particulate phases of OCPs and PCBs, and the average gas/particulate values are summarized in Table 1. The air concentrations of total OCPs (sum of 15 OCPs) were in the range of 47.3–501 pg/m<sup>3</sup>, with a mean of 191 ± 107 pg/m<sup>3</sup>. The average ratios in gaseous phase versus particulate phase of individual OCPs were varied from 8.9 to 1510, indicating that OCPs were largely distributed in the gaseous phase. The average concentrations of most targeted OCPs (e.g.  $\alpha$ -HCH,  $\gamma$ -HCH, *o,p'*-DDD, *p,p'*-DDD, *p,p'*-DDE, TC, CC, and  $\alpha$ -endosulfan) at JSH were lower than or at the same levels as those measured at other background/rural sites (Table 2).

The air concentrations of total PCBs (sum of 32 congeners) varied from 3.40 to 115 pg/m<sup>3</sup>, with an average of 39.4 ± 27.1 pg/m<sup>3</sup>, which was considerably lower than the average air concentration of global background sites (82 (5.1–670) pg/m<sup>3</sup>) (Li et al., 2010). This is consistent with the fact that technical PCBs were not widely used in China in the past. Twelve PCB congeners (PCB 8, 28, 37, 44, 49, 52, 60, 66, 70, 74, 101, and 118) with comparatively high concentrations

both in the gaseous phase (more than 0.45 pg/m<sup>3</sup>) and particulate phase (more than 0.01 pg/m<sup>3</sup>) were selected and shown in Table 1. Similar to OCPs, the gaseous phase concentrations of PCBs accounted for the majority (57%–98%) of the air concentrations, while the particulate phase concentrations of PCBs were fairly low (from non-detectable to 0.38 pg/m<sup>3</sup>), with the average gas/particulate values varied from 19 to 941 (Table 1).

Compared with particulate phases, the gaseous phase concentrations of OCPs and PCBs were much higher (see Table 1). In addition, OCPs and PCBs in particle phase were not detected in several samples (the detection rates of each particle concentration were listed in Table S1). Among them, the detection rates of endosulfans and higher chlorinated PCBs were comparable low. Therefore, the following discussion of atmospheric concentrations, seasonal variations, temperature dependences and air–soil exchanges are based on the gaseous phase concentrations. The particle phase concentrations and their seasonal variations of OCPs and PCBs were discussed in supporting information (Figs. S1–S4).

##### 3.1.1. HCHs

The detection rates of four HCHs (see Table 1) in the gaseous phase were all 100%. The mean concentrations of  $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -

**Table 1**

The average concentrations and ranges of gas phase, particulate phase, and total OCPs and PCBs and the average Gas/Particulate values.

Compounds	Gas (pg/m <sup>3</sup> )	Particulate (pg/m <sup>3</sup> )	Total air concentration (pg/m <sup>3</sup> )	Gas/Particulate
$\alpha$ -HCH	9.48 ± 5.73 (2.34–24.3)	0.03 ± 0.04 (ND–0.20)	9.51 ± 5.72 (2.38–24.3)	1501 ± 3510 (11–17070)
$\beta$ -HCH	2.11 ± 1.72 (0.23–6.85)	0.05 ± 0.06 (ND–0.41)	2.16 ± 1.72 (0.34–9.98)	233 ± 776 (1.9–4631)
$\gamma$ -HCH	4.50 ± 3.15 (0.48–13.8)	0.03 ± 0.04 (ND–0.21)	4.53 ± 3.15 (0.69–13.8)	408 ± 1328 (2.8–8022)
$\delta$ -HCH	0.88 ± 0.62 (0.07–2.96)	0.02 ± 0.02 (ND–0.09)	0.90 ± 0.62 (0.08–2.99)	487 ± 942 (2.3–6305)
$\Sigma$ HCHs <sup>a</sup>	17.0 ± 10.0 (3.12–45.9)	0.13 ± 0.11 (0.02–0.53)	17.1 ± 10 (3.65–46.1)	267 ± 336 (5.9–1711)
<i>o,p'</i> -DDD	0.73 ± 0.56 (0.06–2.30)	0.08 ± 0.07 (<DL–0.41)	0.80 ± 0.54 (0.17–2.35)	19 ± 28 (0.36–173)
<i>p,p'</i> -DDD	0.68 ± 0.58 (0.04–2.26)	0.18 ± 0.18 (0.03–1.16)	0.85 ± 0.57 (0.25–2.52)	8.9 ± 12 (0.13–75)
<i>o,p'</i> -DDE	1.59 ± 1.23 (0.07–5.97)	0.04 ± 0.05 (ND–0.29)	1.63 ± 1.24 (0.17–6.02)	91 ± 152 (0.72–720)
<i>p,p'</i> -DDE	10.4 ± 11.0 (0.32–63.1)	0.31 ± 0.37 (0.02–2.39)	10.7 ± 11.0 (1.43–63.5)	74 ± 94 (0.23–487)
<i>o,p'</i> -DDT	4.29 ± 4.03 (0.09–20.0)	0.37 ± 0.45 (0.02–2.18)	4.66 ± 3.99 (0.51–20.4)	41 ± 54 (0.19–237)
<i>p,p'</i> -DDT	4.49 ± 4.09 (0.12–15.5)	0.40 ± 0.85 (ND–1.68)	4.89 ± 4.21 (0.26–17.1)	18 ± 23 (0.44–142)
$\Sigma$ DDTs <sup>b</sup>	22.1 ± 20.6 (0.71–108)	1.38 ± 1.03 (0.30–5.55)	23.6 ± 20.5 (3.33–111)	27 ± 29 (0.27–134)
TC	5.35 ± 4.18 (0.56–16.1)	0.66 ± 0.45 (0.06–2.04)	6.01 ± 4.28 (0.83–18.1)	13 ± 26 (0.4–201)
CC	2.90 ± 2.01 (0.19–8.22)	0.28 ± 0.15 (ND–0.73)	3.18 ± 2.03 (0.67–8.85)	14 ± 16 (0.39–94)
$\Sigma$ Chlordane <sup>c</sup>	8.24 ± 6.13 (0.75–23.4)	0.94 ± 0.54 (0.12–2.48)	9.18 ± 6.24 (1.52–25.4)	12 ± 20 (0.58–146)
$\alpha$ -endosulfan	4.00 ± 5.37 (<DL–29.8)	0.15 ± 0.26 (ND–1.23)	4.19 ± 5.37 (0.03–29.9)	89 ± 216 (0.42–1010)
$\beta$ -endosulfan	3.44 ± 3.37 (ND–11.9)	0.18 ± 0.24 (ND–1.28)	3.62 ± 3.42 (ND–12.4)	43 ± 74 (0.24–370)
$\Sigma$ Endosulfan <sup>d</sup>	7.44 ± 8.25 (0.22–38.8)	0.33 ± 0.41 (ND–2.51)	7.82 ± 8.32 (0.26–39.1)	41 ± 72 (1.2–375)
HCB	133 ± 122 (17.4–477)	0.53 ± 0.48 (ND–2.53)	133 ± 122 (17.7–479)	372 ± 502 (8.6–2877)
$\Sigma_{15}$ OCPs <sup>e</sup>	188 ± 107 (45.0–496)	3.31 ± 1.55 (ND–8.1)	191 ± 107 (47.3–501)	67 ± 48 (12–302)
PCB8	3.31 ± 3.39 (0.29–17.6)	0.01 ± 0.01 (ND–0.03)	3.43 ± 3.48 (0.31–17.5)	360 ± 492 (13–2766)
PCB28	14.8 ± 12.4 (0.95–44.7)	0.06 ± 0.03 (<DL–0.16)	15.3 ± 12.6 (1.03–44.9)	317 ± 283 (11–1284)
PCB37	1.98 ± 1.55 (0.11–9.48)	0.02 ± 0.02 (ND–0.11)	2.04 ± 1.59 (0.11–9.49)	672 ± 1445 (5.4–7761)
PCB44	2.17 ± 1.83 (0.14–10.7)	0.02 ± 0.05 (ND–0.39)	2.24 ± 1.87 (0.18–10.7)	863 ± 1891 (3.5–10020)
PCB49	2.08 ± 1.65 (0.13–8.55)	0.04 ± 0.03 (ND–0.13)	2.18 ± 1.69 (0.18–8.59)	87 ± 156 (2.6–1158)
PCB52	2.85 ± 2.06 (0.21–10.8)	0.02 ± 0.02 (ND–0.17)	2.94 ± 2.10 (0.24–10.8)	941 ± 2727 (5–15379)
PCB60	1.64 ± 1.45 (0.08–9.05)	0.03 ± 0.03 (ND–0.14)	1.71 ± 1.48 (0.12–9.14)	226 ± 345 (2.4–1526)
PCB66	1.79 ± 1.51 (0.07–9.34)	0.02 ± 0.01 (ND–0.06)	1.85 ± 1.55 (0.10–9.35)	265 ± 651 (2.3–4637)
PCB70	1.87 ± 1.44 (0.11–8.73)	0.02 ± 0.02 (ND–0.09)	1.93 ± 1.47 (0.20–8.73)	603 ± 1780 (1.1–10005)
PCB74	1.49 ± 1.02 (0.10–5.82)	0.01 ± 0.02 (ND–0.13)	1.53 ± 1.04 (0.11–5.82)	518 ± 862 (7.2–3789)
PCB101	0.64 ± 0.36 (0.03–2.10)	0.01 ± 0.02 (ND–0.15)	0.66 ± 0.36 (0.04–2.10)	163 ± 296 (1.6–1485)
PCB118	0.46 ± 0.25 (0.02–1.18)	0.03 ± 0.05 (ND–0.38)	0.49 ± 0.27 (0.08–1.18)	73 ± 100 (0.34–467)
Tri-CBs	17.3 ± 13.9 (1.06–49.2)	0.08 ± 0.05 (0.02–0.24)	17.3 ± 13.9 (1.14–49.4)	304 ± 285 (12–1362)
Tetra-CBs	14.5 ± 10.9 (0.86–61.4)	0.16 ± 0.12 (0.02–0.67)	14.7 ± 10.9 (1.17–61.5)	157 ± 207 (2.8–1084)
Penta-CBs	2.45 ± 1.35 (0.14–6.63)	0.10 ± 0.20 (ND–1.39)	2.54 ± 1.36 (0.28–6.68)	123 ± 180 (0.98–778)
Hexa-CBs	0.77 ± 0.47 (<DL–2.27)	0.12 ± 0.29 (ND–2.07)	0.89 ± 0.56 (0.12–3.17)	65 ± 112 (0.08–431)
Hepta-CBs	0.35 ± 0.30 (0.02–1.29)	0.16 ± 0.42 (ND–3.01)	0.52 ± 0.52 (0.07–3.39)	19 ± 32 (0.13–141)
$\Sigma_{32}$ PCBs	38.8 ± 27.3 (2.61–115)	0.63 ± 1.00 (0.10–7.36)	39.4 ± 27.1 (3.40–115)	136 ± 132 (3–549)

ND: not detected.

DL: detection limit.

<sup>a</sup>  $\Sigma$ HCHs =  $\alpha$ -HCH +  $\beta$ -HCH +  $\delta$ -HCH +  $\gamma$ -HCH.

<sup>b</sup>  $\Sigma$ DDTs = *p,p'*-DDE + *p,p'*-DDD + *o,p'*-DDT + *p,p'*-DDT.

<sup>c</sup>  $\Sigma$ Chlordane = TC + CC.

<sup>d</sup>  $\Sigma$ Endosulfan =  $\alpha$ -endosulfan +  $\beta$ -endosulfan.

<sup>e</sup>  $\Sigma_{15}$ OCPs =  $\Sigma$ HCHs +  $\Sigma$ DDTs +  $\Sigma$ Chlordane +  $\Sigma$ Endosulfan + HCB.



**Table 2**Comparison of mean atmospheric OCP concentrations ( $\text{pg}/\text{m}^3$ ) at JSH station with those in other background and rural sites.

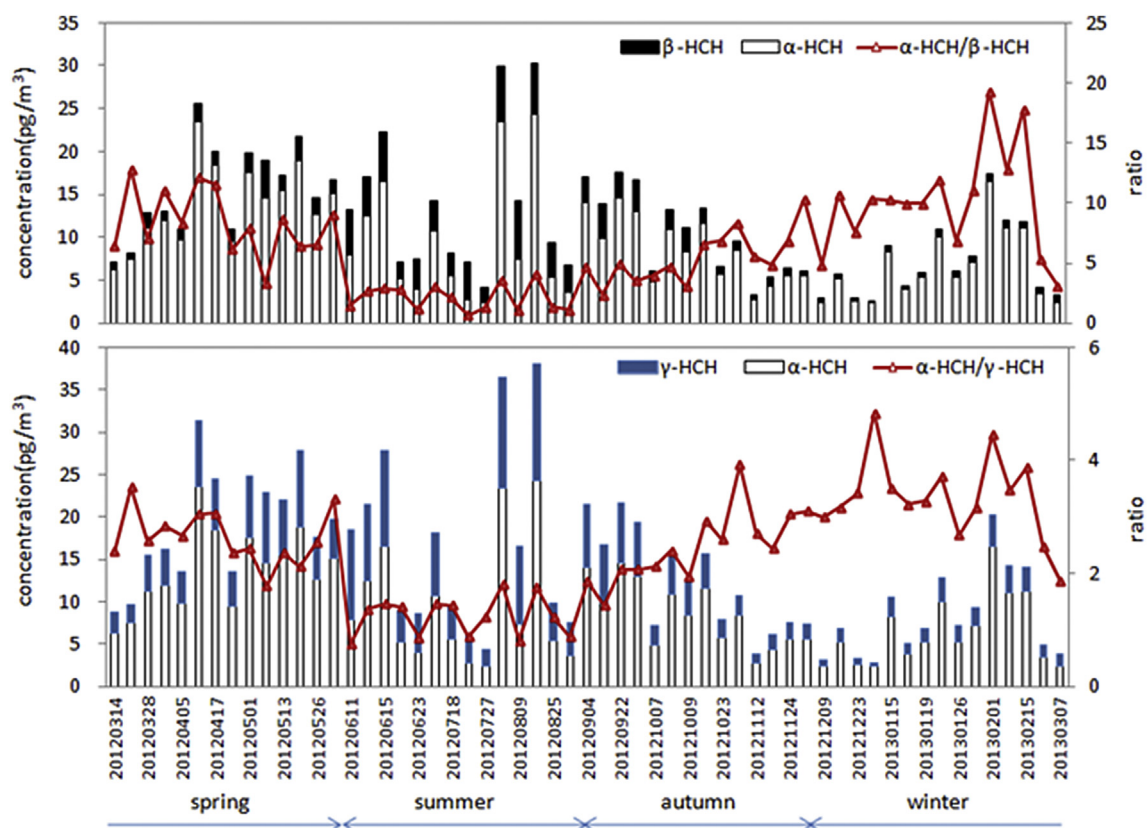
	$\alpha$ -HCH	$\gamma$ -HCH	$\alpha,p'$ -DDT	$p,p'$ -DDT	$p,p'$ -DDE	TC	CC	$\alpha$ -endosulfan	HCB
JSH (this study)	9.48	4.50	4.29	4.49	10.4	5.35	2.90	4.00	133
Ningbo <sup>a</sup>	16.7	1.5	17.7	14.3	13.3	10.5	38.7	–	21.6
Tengchong <sup>b</sup>	42	130	11	20	6.1	40	59	42	270
Alert <sup>c</sup> ,2005	13	1.7	0.22	0.14	0.3	0.25	0.64	5.6	52
Zeppelin <sup>c</sup> ,2006	11	1.9	0.21	0.11	1.2	0.22	0.61	–	72
Tibetan Plateau <sup>d</sup>	91	15.8	13.4	6.13	0.64	0.04	0.03	97.3	23.3
Mt. Waliguan <sup>e</sup>	58.4	139	17.9	4.42	5.12	18.1	22.1	–	38.4
Mt. Everest <sup>f</sup>	19.2	7.7	5.1	3.7	5.1	–	–	27.6	8.9

<sup>a</sup> 2009.7–2010.3 (Liu et al., 2014).<sup>b</sup> 2005.10–2006.12 (Xu et al., 2011).<sup>c</sup> 2005 (Hung et al., 2010).<sup>d</sup> 2007.07–2008.06 (Xiao et al., 2010).<sup>e</sup> 2005.04.22–05.23 (Cheng et al., 2007).<sup>f</sup> 2002.03.31–36.11 (Li et al., 2006).

HCH and  $\delta$ -HCH were  $9.48 \pm 5.73$ ,  $2.11 \pm 1.72$ ,  $4.50 \pm 3.15$  and  $0.88 \pm 0.62$   $\text{pg}/\text{m}^3$ , respectively. As shown in Table 2, the average concentrations of  $\alpha$ -HCH and  $\gamma$ -HCH were lower than those of the other background sites in China, such as Tengchong ( $\alpha$ -HCH, 42  $\text{pg}/\text{m}^3$ ;  $\gamma$ -HCH, 130  $\text{pg}/\text{m}^3$ ), Tibetan Plateau ( $\alpha$ -HCH, 91  $\text{pg}/\text{m}^3$ ;  $\gamma$ -HCH, 15.8  $\text{pg}/\text{m}^3$ ), Mt. Waliguan ( $\alpha$ -HCH, 58.4  $\text{pg}/\text{m}^3$ ;  $\gamma$ -HCH, 139  $\text{pg}/\text{m}^3$ ), and Mt. Everest ( $\alpha$ -HCH, 19.2  $\text{pg}/\text{m}^3$ ;  $\gamma$ -HCH, 7.7  $\text{pg}/\text{m}^3$ ) (Li et al., 2006; Cheng et al., 2007; Xiao et al., 2010; Xu et al., 2011).

The  $\alpha$ -HCH in the environment is mainly from the historical usage of technical HCH, and it accounts for about 60–70% of total technical HCH.  $\beta$ -HCH is another isomer in technical HCH that accounts for 5–12% of technical HCH, and it is characterized by the strongest resistance to degradation (Burgoyne and Hites, 1993; Li et al., 1996; Liu et al., 2014). High  $\alpha/\beta$ -HCH ratios usually indicate

the current sources of technical HCH while low ratios suggest the historical sources. The average  $\alpha/\beta$ -HCH ratio was  $6.23 \pm 4.06$  at JSH, which was close to the lower limit of technical mixture (5–14), indicating the characteristic of residual technical HCH. However, owing to the relatively low  $\beta$ -HCH concentrations and high  $\alpha$ -HCH concentrations, higher  $\alpha/\beta$ -HCH ratios (from 4.21 to 19.33) were observed in winter (Fig. 2). China banned the production and use of technical HCH in 1983; therefore, the high levels of atmospheric  $\alpha$ -HCH in winter mainly originated from LRAT.  $\alpha$ -HCH is more likely to be involved in the process of LRAT compared with  $\beta$ -HCH, and  $\gamma$ -HCH can be transformed into  $\alpha$ -HCH under direct sunlight during the process of LRAT (Malaiyandi and Shah, 1984). Backward trajectories at JSH during the sampling period suggested that air masses in winter were from Northeast and Northwest China (Zhang

**Fig. 2.** Seasonal variation of  $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH and isomeric ratios.

et al., 2014). Thus, the high concentration levels of  $\alpha$ -HCH at JSH in winter were attributed to polluted air parcels originating from northern China. Similar results were observed in the observation site of the coastal East China Sea (Ji et al., 2015).

The ratio of  $\alpha/\gamma$ -HCH is used to trace the emission source of technical HCH and lindane. Lindane contains more than 90% of  $\gamma$ -HCH (Li et al., 1996). In general, the average  $\alpha/\gamma$ -HCH ratio between 3:1 and 7:1 (Tsunogai and Henmi, 2002) indicates the usage or residue of technical HCH, and the input of lindane can reduce the value of the  $\alpha/\gamma$ -HCH ratio. The average  $\alpha/\gamma$ -HCH ratio was  $2.41 \pm 0.89$  at JSH, higher than that in Tengchong ( $0.56 \pm 0.48$ ) and Mt. Waliguan ( $0.48 \pm 0.27$ ) (Cheng et al., 2007; Xu et al., 2011) but lower than that of the technical mixture (3–7), suggesting that lindane rather than technical HCH represented the primary contribution. Similarly, the relatively high  $\alpha/\gamma$ -HCH ratios in winter (Fig. 2) were also related to the transformation from  $\gamma$ -HCH to  $\alpha$ -HCH during LRAT.

### 3.1.2. DDTs

The detection rates of six DDTs (see Table 1) in the gaseous phase were all 100%. The total gaseous concentrations of six DDTs ranged from 0.71 to 108  $\text{pg}/\text{m}^3$  in the atmosphere of JSH. The top three homologues in terms of concentrations were *p,p'*-DDE, *p,p'*-DDT and *o,p'*-DDT, with mean values of  $10.4 \pm 11.0$ ,  $4.49 \pm 4.09$  and  $4.29 \pm 4.03$   $\text{pg}/\text{m}^3$ , respectively. As shown in Table 2, the mean concentration of *p,p'*-DDT at JSH was similar to that in the Tibetan Plateau (*p,p'*-DDT, 6.13  $\text{pg}/\text{m}^3$ ; *p,p'*-DDE, 0.64  $\text{pg}/\text{m}^3$ ; *o,p'*-DDT, 13.4  $\text{pg}/\text{m}^3$ ), Mt. Waliguan (*p,p'*-DDT, 4.42  $\text{pg}/\text{m}^3$ ; *p,p'*-DDE, 5.12  $\text{pg}/\text{m}^3$ ; *o,p'*-DDT, 17.9  $\text{pg}/\text{m}^3$ ), and Mt. Everest (*p,p'*-DDT, 3.7  $\text{pg}/\text{m}^3$ ; *p,p'*-DDE, 5.1  $\text{pg}/\text{m}^3$ ; *o,p'*-DDT, 5.1  $\text{pg}/\text{m}^3$ ), whereas the mean concentration of *p,p'*-DDE was higher and *o,p'*-DDT was lower when compared to the aforementioned sites (Li et al., 2006; Cheng et al., 2007; Xiao et al., 2010).

The ratio of *o,p'*-DDT/*p,p'*-DDT often acts as a symbol for distinguishing the sources of DDTs from technical DDT and dicofol. Technical DDT includes less *o,p'*-DDT than *p,p'*-DDT, while the dicofol-type DDT pollution is characterized by high values of *o,p'*-DDT/*p,p'*-DDT (Qiu et al., 2005). The average *o,p'*-DDT/*p,p'*-DDT ratio was  $0.97 \pm 0.15$  at JSH, which was comparable to the range of technical DDT (0.74–0.96) (Liu et al., 2009), implying the input of DDT at JSH was dominated by technical DDT. *p,p'*-DDE is the degradation product of *p,p'*-DDT, and the ratio of *p,p'*-DDT/*p,p'*-DDE is often used to identify previous usage or current input of DDT. The average *p,p'*-DDT/*p,p'*-DDE ratio at JSH was  $0.45 \pm 0.24$ , which was comparable with that of Amderma (0.51–0.81) (Hung et al., 2010), indicating the atmospheric DDTs at JSH were mainly from aged technical DDT.

### 3.1.3. Chlordanes

The concentrations of chlordane (TC + CC) in the gaseous phase ranged from 0.75 to 23.4  $\text{pg}/\text{m}^3$  at JSH. The mean concentrations of individual compounds were  $5.35 \pm 4.18$   $\text{pg}/\text{m}^3$  for TC and  $2.90 \pm 2.01$   $\text{pg}/\text{m}^3$  for CC, respectively. These values were rather lower than those from Ningbo, Tengchong and Mt. Waliguan (Cheng et al., 2007; Xu et al., 2011; Liu et al., 2014), but higher than those in the Arctic (Hung et al., 2010) (Table 2). The ratio of TC/CC has been used to identify the “age” of the substance (Halsall et al., 1998). Generally, the ratio of TC/CC in technical chlordane is 1.1–1.3, and TC is more sensitive to photo-degradation than CC in the environment (Bidleman et al., 2002; Hung et al., 2002). The average ratio of TC/CC at JSH was  $1.77 \pm 0.37$ , which was higher than that of technical mixture and other background regions (Ningbo 0.33–1.09, Tengchong 0.64  $\pm$  0.34) (Xu et al., 2011; Liu et al., 2014), suggesting fresh input to the atmosphere. It is known that technical chlordane usually contains about 5% of heptachlor (Bidleman et al.,

2002), and technical heptachlor is often mixed with chlordane isomers, especially TC (Hung et al., 2002). In addition, current usage of chlordane as mirex was found in China, especially in east, north and central China (Wang et al., 2013). Thus, the atmospheric chlordane and higher ratios of TC/CC at JSH suggest the fresh input of pesticides (such as chlordane and heptachlor).

### 3.1.4. Endosulfans

Technical endosulfan contains about 70% of  $\alpha$ -endosulfan and 30% of  $\beta$ -endosulfan (Burgoyne and Hites, 1993). The measured gaseous phase concentrations of two endosulfans ranged from 0.22 to 38.8  $\text{pg}/\text{m}^3$  at JSH, and the average concentrations of  $\alpha$ -endosulfan and  $\beta$ -endosulfan were  $4.00 \pm 5.37$  and  $3.44 \pm 3.37$   $\text{pg}/\text{m}^3$ , respectively. The mean concentration of  $\alpha$ -endosulfan was similar to that observed in the Arctic (Hung et al., 2010) but lower than that of Mt. Everest and Tengchong (Li et al., 2006; Xu et al., 2011) (Table 2). The average  $\alpha/\beta$ -endosulfan ratio was  $1.09 \pm 0.58$ , which was lower than that of the technical mixture (7:3). This was because of the faster photo-degradation rate of  $\alpha$ -endosulfan in atmosphere, indicating no fresh input of endosulfan at JSH (Sutherland et al., 2004).

### 3.1.5. HCB

HCB is generated as a by-product and/or impurity of the chlorination manufacturing processes, and emissions from incomplete combustion. The release of aged HCB from soils and water could also contribute to its ambient air level (Barber et al., 2005). The concentration of HCB in the gaseous phase of JSH ranged from 17.4 to 477  $\text{pg}/\text{m}^3$ , with an average of  $133 \pm 122$   $\text{pg}/\text{m}^3$ , which was about a half of that in Tengchong ( $270 \pm 100$   $\text{pg}/\text{m}^3$ ) (Xu et al., 2011) but higher than that in Ningbo, Mt. Waliguan, Mt. Everest, and the Arctic (Li et al., 2006; Cheng et al., 2007; Hung et al., 2010; Liu et al., 2014) (Table 2).

### 3.1.6. PCBs

The relatively higher concentration levels were observed for PCB 8, 28, 37, 44, 49, 52, 60, 66, 70, 74, 101, 118, with the average gaseous concentrations from 0.46 to 14.8  $\text{pg}/\text{m}^3$  (Table 1). As ones of indicator PCBs, the average concentrations of PCB 28, PCB 52, PCB 101, and PCB 118 were  $14.8 \pm 12.4$ ,  $2.85 \pm 2.06$ ,  $0.64 \pm 0.36$  and  $0.46 \pm 0.25$   $\text{pg}/\text{m}^3$ , respectively. PCB 28 was the most prominent individual PCB congener in this study, with a higher average concentration than those of the other ten background sites (except for Site D) of China (Table S2) (Wu et al., 2011). Moreover, the mean concentrations of PCB 52, PCB 101 and PCB 118 in the atmosphere at JSH were comparable with those in the central China background site (Site D) (Table S2) (Wu et al., 2011). The average concentrations of tri-, tetra-, penta-, hexa-, and hepta-CBs were  $17.3 \pm 13.9$ ,  $14.5 \pm 10.9$ ,  $2.45 \pm 1.35$ ,  $0.77 \pm 0.47$  and  $0.35 \pm 0.30$   $\text{pg}/\text{m}^3$ , respectively (Table 1). The sum of tri-CBs and tetra-CBs in the atmosphere accounted for nearly 70% of the total PCBs. These results were consistent with the homolog composition of the Chinese PCB products and usages, which mainly consist of tri-PCB followed by tetra-PCB (Ren et al., 2007).

## 3.2. Seasonal variations and temperature dependence of atmospheric OCPs and PCBs

Seasonal variations of representative OCPs and PCBs were observed from Fig. 2 to Fig. 7. Significant seasonal characteristics of *o,p'*-DDT, *p,p'*-DDT, *p,p'*-DDE, and endosulfans were observed in Figs. 3 and 5, respectively, with high concentrations in summer and low concentrations in winter. The highest concentrations of the three DDT homologues were observed in August while those of endosulfans were both exhibited in September. The concentrations

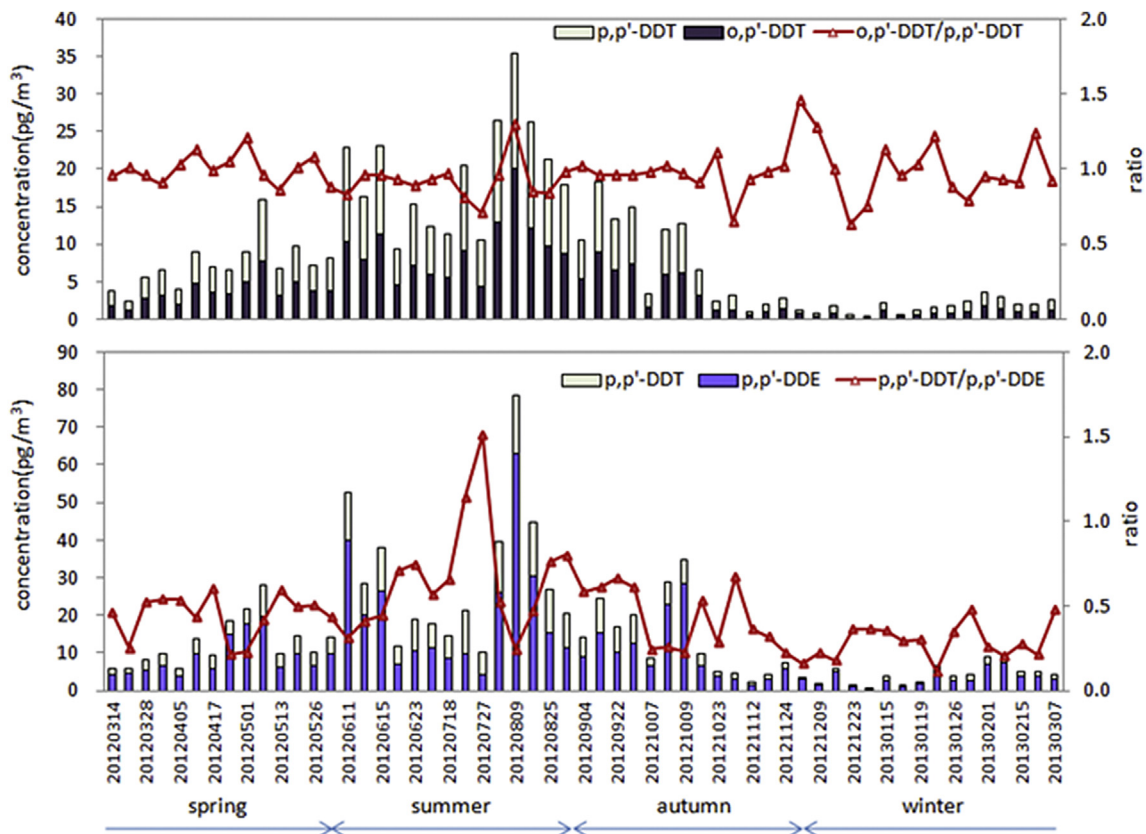


Fig. 3. Seasonal variation of *o,p'*-DDT, *p,p'*-DDT, *p,p'*-DDE and isomeric ratios.

of  $\alpha$ -HCH,  $\gamma$ -HCH, and  $\beta$ -HCH showed the same seasonal variation, high in spring and summer (with the maximum concentrations appeared in summer), declining in autumn but increasing in winter (Fig. 2). The seasonal variations of chlordanes showed that TC and CC concentrations were observed elevated in spring and summer but decreased in autumn and winter (Fig. 4). The concentrations of HCB displayed an opposite seasonal trend to other OCPs, high in winter but low in summer, with an average of  $285 \pm 131 \text{ pg/m}^3$  in winter and  $37.5 \pm 15.7 \text{ pg/m}^3$  in summer. In addition, the concentrations of HCB in spring and autumn were also higher than those in summer (Fig. 6). Seasonal variations of the four PCBs were shown in Fig. 7. The concentrations of PCB 28 and PCB 52 exhibited significant

seasonal variations, with the maximum occurred in summer and the minimum appeared in winter. In contrast, no obvious seasonal variation was found for PCB 101 and PCB 118.

If the amount of OCPs and PCBs present in the atmosphere is controlled by temperature-dependent volatilization from soils and water bodies, the measured concentrations should be related to the ambient temperature (Mandalakis and Stephanou, 2007). This gaseous-phase behavior of OCPs and PCBs was described in terms of the Clausius–Clapeyron equation (Wania et al., 1998):

$$\ln P = -\Delta H/RT + C = m/T + b$$

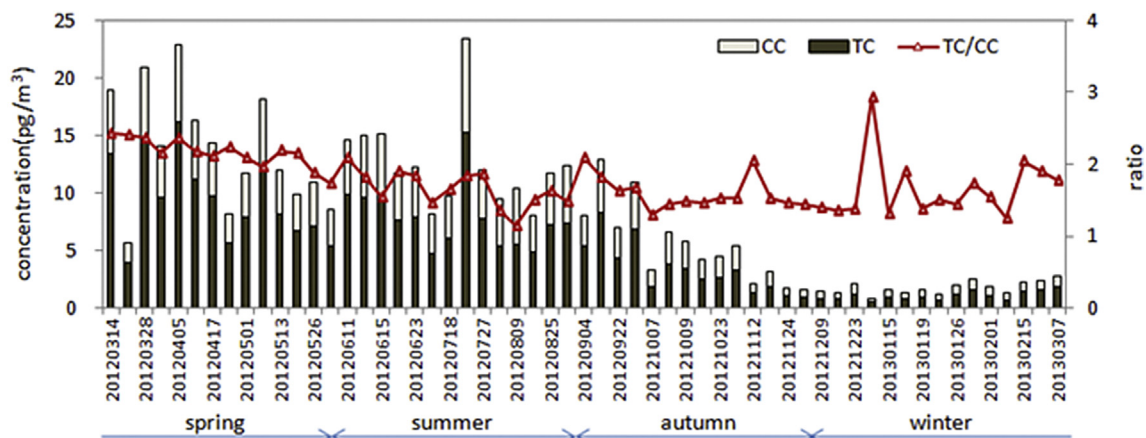


Fig. 4. Seasonal variation of chlordanes concentrations and TC/CC ratios.

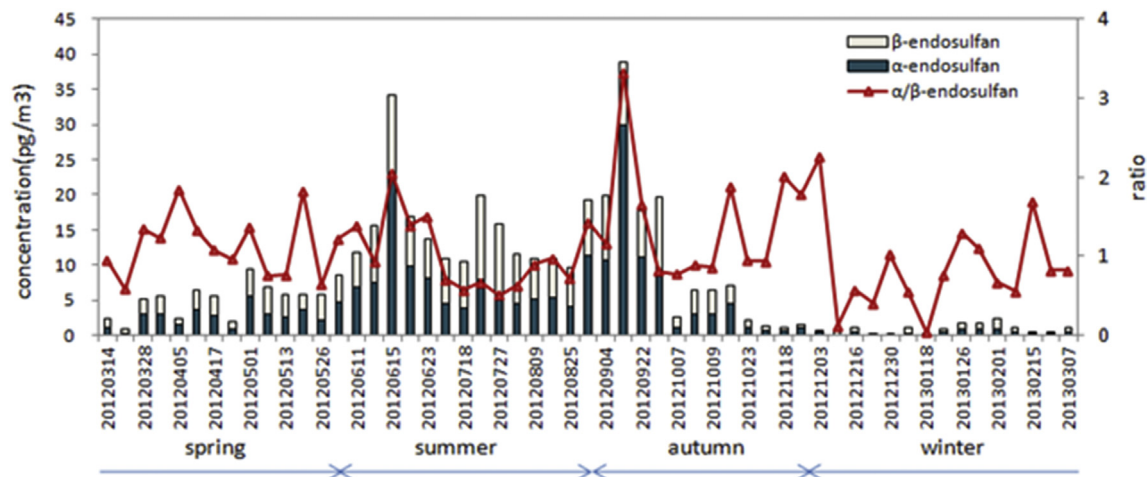


Fig. 5. Seasonal variation of endosulfan concentrations.

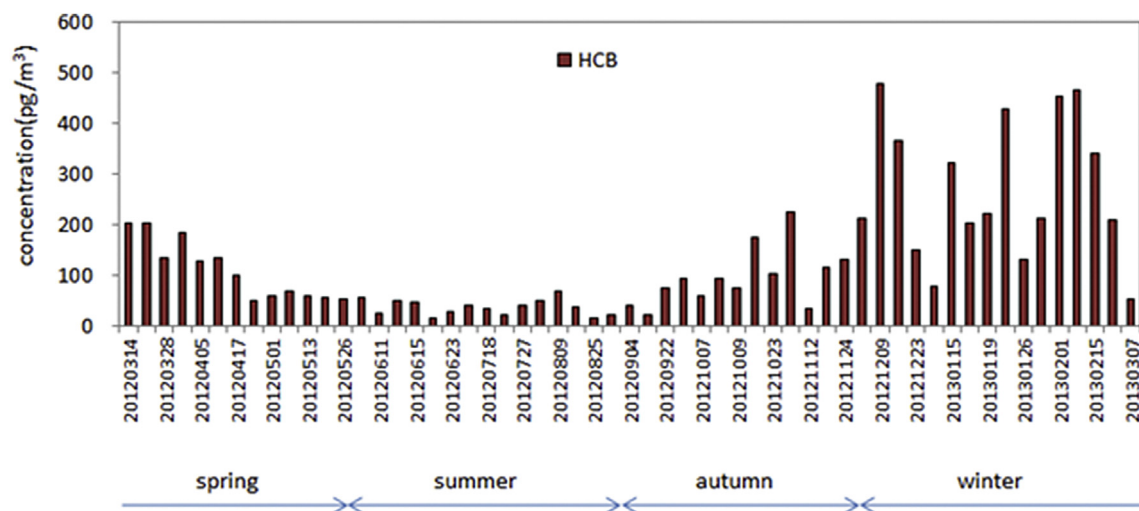


Fig. 6. Seasonal variation of HCB concentrations.

where  $P$  is the partial vapor pressure (atm),  $\Delta H$  is the enthalpy of vaporization ( $\text{kJ/mol}^{-1}$ ),  $T$  is the ambient temperature (K),  $m$  is the slope, and  $b$  is the intercept of the line. The gas-phase concentrations of OCPs and PCBs were converted into partial pressures using the ideal gas law and their molecular weights. Subsequently, the natural logarithms of the partial pressures were regressed against the reciprocal mean temperature of the sampling events.

Regression results for individual OCPs and selected PCB congeners are summarized in Table 3. A steep negative slope and high  $R^2$  values suggests that the contaminants in the air were largely controlled by evaporation from surfaces around the sampling site, whereas a shallow negative slope indicates that the contaminants in the air were principally influenced by the LRAT, and the positive slope may be attributed to ongoing sources (Wania et al., 1998; Sofuoglu et al., 2004).

For most of OCPs and PCBs, the temperature dependences of their gas-phase concentrations were statistically significant ( $p < 0.05$ ) (Table 3). The slopes for all OCPs (except for HCB) and PCBs were negative. Strong temperature dependences were observed for  $o,p'$ -DDT,  $p,p'$ -DDT and endosulfans, with steep slopes ranging from  $-10,664$  to  $-13,667$  (with high  $R^2$  values between 0.729 and 0.821), indicating the possible contribution of surfaces

volatilization. The relatively shallow slopes for HCHs and chlor-danes (ranged from  $-2178$  to  $-7858$ ) implied the LRAT to JSH. The positive slope (6843) of HCB, which was different from other OCPs, suggested the influence of strong fresh input or ongoing sources, especially in winter (Sofuoglu et al., 2004). The JSH site is located on an isolated mountain peak with several inhabitants on the surrounding mountains. Therefore, the ongoing sources of HCB were related to the combustion processes around the sampling site. The slopes of selected PCB congeners with 3–7 chlorine atoms were between  $-3124$  and  $-7127$  with  $R^2$  values from 0.208 to 0.654 (Table 3). Lower chlorinated PCBs were more dependent on temperature than higher chlorinated PCBs, especially tri-CBs and tetra-CBs. Overall, the shallow slopes and low  $R^2$  values of PCBs suggested that the air concentrations of PCBs were attributed to the LRAT.

### 3.3. OCPs and PCBs concentrations in soil

Table 4 shows the average concentrations, ranges and H/L values (the ratio of highest to lowest concentration) of OCPs and selected PCBs in soil samples. Concentrations of OCPs and selected PCBs in each soil sample were given in Tables S3 and S4. The average concentration with standard deviation for total OCPs (sum of 15



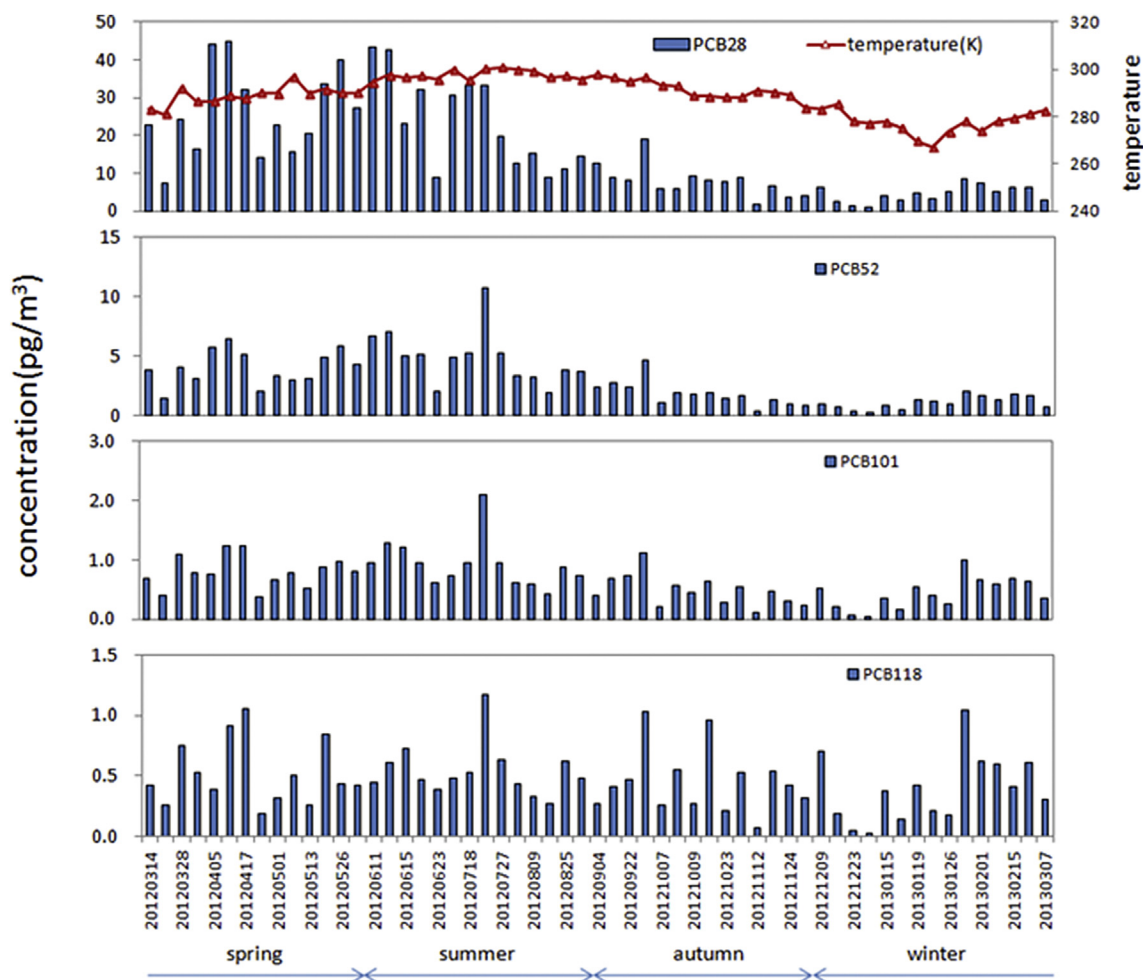


Fig. 7. Seasonal variation of selected PCBs (PCB28, 52, 101, 118) and the ambient temperature over the entire sampling campaign.

OCPs) was  $0.585 \pm 0.437$  ng/g. Among these compounds, the mean concentration of total DDTs (sum of 6 DDTs) was very high in the soil samples, reaching up to  $0.303 \pm 0.258$  ng/g and ranging from 0.034 to 0.904 ng/g. All the metabolites of DDT were presented in the soil, but *p,p'*-DDT exhibited the highest mean concentration of  $0.154 \pm 0.146$  ng/g, which contributed more than 50% of the total DDTs. The concentration levels of HCB were the second highest, with a mean value of  $0.162 \pm 0.093$  ng/g and ranging from 0.046 to 0.352 ng/g, reaching a peak in spring (Table S3). The measured chlordane concentrations were 0.008–0.142 ng/g for TC and 0.005–0.113 ng/g for CC, with relatively high levels in spring and summer, which was similar to the seasonal variation in air. The targeted compounds with low concentration level include HCHs and endosulfans. The average concentration of total HCHs (sum of 4 HCHs) was  $0.041 \pm 0.033$  ng/g, and the average concentrations for  $\alpha$ -HCH,  $\beta$ -HCH, and  $\gamma$ -HCH were all in the same order of magnitude (between 0.10 and 0.20 ng/g) (Table 4). The concentration of endosulfans was the lowest of the studied compounds with an average value of  $0.018 \pm 0.014$  ng/g. Overall, compared with previous studies, the concentrations of OCPs in soil samples at JSH were lower than other regions, such as the Tibetan Plateau (DDTs, 13–7700 pg/g; HCHs, 64–847 pg/g; HCB, 24–564 pg/g) (Wang et al., 2012b), the Southern United States (DDTs, 0.10–1490 ng/g; HCHs, 0.05–0.71 ng/g; Chlordane, 0.05–5.1 ng/g) (Bidleman and Leone, 2004), and Punjab, Pakistan (DDTs,  $40 \pm 60$  ng/g; HCHs,  $7.8 \pm 5.5$  ng/g; Chlordane,  $3.8 \pm 2.0$  ng/g; HCB,  $1.9 \pm 3.0$  ng/g) (Syed

et al., 2013a).

Differences of 1 or 2 orders of magnitude were observed for all H/L values of OCPs (Table 4). The extremely high H/L values of DDTs were related to the highest soil concentration that occurred in August and the lowest in November (Table S3), which may indicate fresh DDT input (see Section 3.4). The JSH site is located on an isolated mountain peak with several inhabitants and farmland in the surrounding areas. Therefore, elevated soil or air concentrations of contaminants at JSH were partly related to the use of pesticides in the surrounding areas, and the high H/L values for DDTs and chlordanes appeared in August, suggesting their fresh inputs in summer. However, the lowest soil concentrations of some OCPs (such as  $\alpha$ -HCH,  $\alpha$ -endosulfan and etc.) were under the detection limits, while others (*p,p'*-DDD, 0.001 ng/g; CC, 0.005 ng/g and etc.) were barely above the detection limits, and the ranges of H/L values were related to their low concentrations and the low signal-to-noise ratio. For these reasons, H/L values of these OCPs were enhanced.

The concentrations of total PCBs (sum of 32 PCBs) in the soil samples varied from 0.033 to 0.160 ng/g, providing an average value of  $0.083 \pm 0.039$  ng/g, which was lower compared with that of Tibet (0.138 ng/g dw) and Zhejiang Province (1.14 ng/g dw) (Ren et al., 2007). The selected PCB congeners which had relatively high average concentrations in the soil were shown in Table 4. The mean concentration of PCB 28 in the soil was  $0.021 \pm 0.010$  ng/g, while that of each else individual PCB congeners was no more than

**Table 3**  
Temperature dependence of OCPs and PCBs in the atmosphere of JSH.

Compounds	N	m	b	R <sup>2</sup>	Significance
α-HCH	57	-2178	9.64	0.110	p < 0.05
β-HCH	57	-7687	27.19	0.799	p < 0.01
γ-HCH	57	-5760	21.31	0.574	p < 0.01
δ-HCH	57	-6135	20.99	0.662	p < 0.01
o,p'-DDD	57	-7375	25.04	0.714	p < 0.01
p,p'-DDD	57	-8648	29.33	0.770	p < 0.01
o,p'-DDE	57	-6541	22.94	0.580	p < 0.01
p,p'-DDE	57	-7567	28.26	0.576	p < 0.01
o,p'-DDT	57	-10444	37.32	0.811	p < 0.01
p,p'-DDT	57	-10533	37.67	0.821	p < 0.01
TC	57	-7858	28.65	0.630	p < 0.01
CC	57	-7820	27.97	0.723	p < 0.01
α-endosulfan	57	-13667	48.10	0.729	p < 0.01
β-endosulfan	57	-12282	43.33	0.734	p < 0.01
HCB	57	6834	19.31	0.561	p < 0.01
PCB28	62	-6364	24.45	0.500	p < 0.01
PCB37	62	-6111	21.63	0.553	p < 0.01
PCB44	62	-7127	25.20	0.648	p < 0.01
PCB49	62	-6937	24.51	0.635	p < 0.001
PCB52	62	-5989	21.59	0.566	p < 0.01
PCB60	62	-5254	18.46	0.436	p < 0.01
PCB66	62	-7121	25.00	0.654	p < 0.01
PCB70	62	-6268	22.13	0.607	p < 0.01
PCB74	62	-4731	16.60	0.382	p < 0.01
PCB101	62	-4502	15.02	0.427	p < 0.01
PCB118	62	-3124	9.90	0.208	p < 0.05
Tri-CBs	62	-6346	24.52	0.512	p < 0.01
Tetra-CBs	62	-6074	23.48	0.573	p < 0.01
Penta-CBs	62	-3797	13.9	0.317	p < 0.01
Hexa-CBs	62	-4114	13.8	0.258	p < 0.05
Hepta-CBs	62	-3301	10.09	0.149	NS
ΣPCBs	62	-5366	22.01	0.471	p < 0.01

N represents the number of samples involved in the calculation.  
NS means non-significant correlation.

0.007 ng/g. The dominant homolog in the soil samples was tetra-CBs followed by tri-CBs, which accounted for almost 80% of the total PCB concentration. This was similar to the finding in Chinese background/rural soil that the levels of lower chlorinated PCBs were high, whereas those of the higher chlorinated PCBs were low (Ren et al., 2007). Moreover, the H/L values of PCBs were less than those of OCPs, with a range from 1.0 to 11, suggesting that there was no fresh input of PCBs at JSH.

### 3.4. Air–soil exchange of OCPs and PCBs

To determine the potential sources of OCPs and PCBs at JSH, the soil and the atmospheric concentrations were measured to infer the direction of air–soil exchange. Fugacity is an effective method used to measure the potential pressure of chemicals between different interfaces and it is proportional to concentration. The fugacity of POPs in soil ( $f_s$ ) and air ( $f_a$ ) was calculated with the following equations (Harner et al., 2001):

$$f_s = C_s RT / 0.411 \phi_{om} K_{oa}$$

$$f_a = C_a RT$$

where  $C_s$  and  $C_a$  are the concentration of POPs in soil and air ( $\text{mol}/\text{m}^3$ ),  $R$  is the gas constant ( $8.314 \text{ pa m}^3 \text{ mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the absolute temperature (K),  $\phi_{om}$  is the fraction of organic matter in the soil on a dry soil basis (1.7 times the organic carbon fraction),  $K_{oa}$  is the octanol-air partition coefficient of the compound. It was assumed that the fugacity capacity of soil was totally attribute to the organic matter fraction and the density of soil bulk was  $1.5 \times 10^6 \text{ g}/\text{m}^3$  (Bidleman and Leone, 2004). The factor 0.411 improves the

**Table 4**  
Basic descriptive analysis for OCPs and PCBs detected in soil samples.

Compounds	Mean $\pm$ std.(ng/g)	Range	H/L
α-HCH	0.012 $\pm$ 0.012	ND–0.036	/
β-HCH	0.016 $\pm$ 0.016	0.004–0.046	10.9
γ-HCH	0.010 $\pm$ 0.007	0.002–0.024	14.9
δ-HCH	0.002 $\pm$ 0.002	ND–0.007	/
ΣHCHs	0.041 $\pm$ 0.033	0.006–0.096	15.2
o,p'-DDD	0.015 $\pm$ 0.014	0.001–0.044	38.2
p,p'-DDD	0.044 $\pm$ 0.043	0.002–0.135	63.8
o,p'-DDE	0.005 $\pm$ 0.003	0.002–0.013	7.3
p,p'-DDE	0.052 $\pm$ 0.033	0.010–0.107	10.3
o,p'-DDT	0.032 $\pm$ 0.027	0.003–0.098	28.1
p,p'-DDT	0.154 $\pm$ 0.146	0.014–0.518	37.0
ΣDDTs	0.303 $\pm$ 0.258	0.034–0.904	26.3
TC	0.048 $\pm$ 0.047	0.008–0.142	16.7
CC	0.032 $\pm$ 0.034	0.005–0.113	22.5
ΣChlordane	0.080 $\pm$ 0.081	0.014–0.254	18.8
α-endosulfan	0.004 $\pm$ 0.003	ND–0.009	/
β-endosulfan	0.014 $\pm$ 0.013	ND–0.043	/
ΣEndosulfan	0.018 $\pm$ 0.014	0.002–0.046	22.9
HCB	0.162 $\pm$ 0.093	0.046–0.352	7.7
Σ <sub>15</sub> OCPs	0.585 $\pm$ 0.437	0.152–1.414	9.3
PCB8	0.006 $\pm$ 0.003	0.002–0.013	6.5
PCB28	0.021 $\pm$ 0.010	0.008–0.038	4.8
PCB37	0.003 $\pm$ 0.001	0.001–0.006	6.0
PCB44	0.005 $\pm$ 0.002	0.002–0.009	4.5
PCB49	0.005 $\pm$ 0.002	0.001–0.011	11.0
PCB52	0.007 $\pm$ 0.004	0.002–0.016	8.0
PCB60	0.004 $\pm$ 0.002	0.001–0.007	7.0
PCB66	0.005 $\pm$ 0.003	0.002–0.012	6.0
PCB70	0.005 $\pm$ 0.003	0.002–0.010	5.0
PCB74	0.003 $\pm$ 0.002	0.001–0.007	7.0
PCB101	0.002 $\pm$ 0.001	0.001–0.004	4.0
PCB118	0.003 $\pm$ 0.002	0.001–0.001	1.0
Tri-CBs	0.030 $\pm$ 0.014	0.012–0.055	4.6
Tetra-CBs	0.035 $\pm$ 0.018	0.013–0.074	5.7
Penta-CBs	0.010 $\pm$ 0.005	0.004–0.021	5.3
Hexa-CBs	0.005 $\pm$ 0.003	ND–0.008	/
Hepta-CBs	0.003 $\pm$ 0.002	ND–0.006	/
Σ <sub>32</sub> PCBs	0.083 $\pm$ 0.039	0.033–0.160	4.8
TOC(g/kg)	9.18 $\pm$ 3.15	5.14–13.9	2.7

TOC: total organic carbon.  
H/L: highest/lowest ratio.

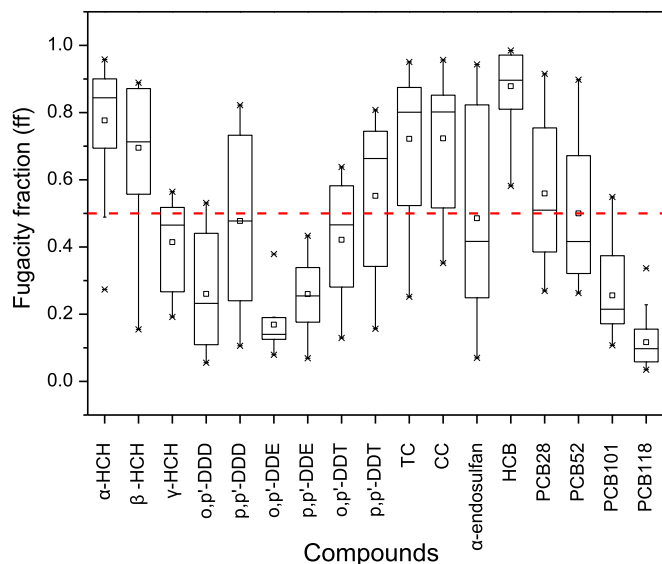
correlation between the soil–air partition coefficient and  $K_{oa}$  (Meijer et al., 2003). The  $K_{oa}$  values of OCPs and PCBs at different temperatures were taken from former studies (Ockenden et al., 2001; Shoeib and Harner, 2002).

The fugacity fraction ( $ff$ ) was calculated from the measured air and soil fugacities:

$$ff = f_s / (f_s + f_a)$$

The value of fugacity fraction is equal to 0.5 indicating the soil–air equilibrium, whereas  $ff > 0.5$  and  $ff < 0.5$  represent net volatilization from soil to air and net deposition from air to soil, respectively. The uncertainty in  $ff$ , which mainly originates from the concentrations in air and soil and the values of  $K_{oa}$ , should be taken into account during the calculation process (Harner et al., 2001). With the uncertainty, the fugacity fractions ( $ff$ ) for selected OCPs and PCB congeners (PCB 28, 52, 101, and 118) were calculated and shown in Fig. 8 and Table S5. In addition, the ratios of contaminants ( $\alpha/\beta$ -HCH,  $\alpha/\gamma$ -HCH,  $o,p'$ -DDT/ $p,p'$ -DDT,  $p,p'$ -DDT/ $p,p'$ -DDE, TC/CC and  $\alpha/\beta$ -endosulfan) in air and soil (Table 5) were also taken into account when evaluating the source–to–sink relationships for each contaminants between soil and air.

The  $ff$  values for different contaminants were dependent on the physical and chemical properties of the individual compounds as well as on residual characteristics or current sources. The  $ff$  values



**Fig. 8.** Fugacity fraction ( $ff$ ) of OCPs and PCBs at JSH. The boxes are defined by the 25th and 75th percentiles; whiskers mark the 10th and 90th percentiles; the median is represented by a horizontal line; the mean by a square; and outliers with an asterisk. Dashed line indicates the limits of  $ff$  for equilibrium.

for OCPs covered a wide range between 0.07 and 0.96, indicating that the soil was not only the source but also the recipient for OCPs. The wide  $ff$  ranges of OCPs were similar to those reported for Pakistan (Syed et al., 2013b) and Europe (Růžicková et al., 2008). In this study, the average  $ff$  values were 0.78 (0.27–0.96) for  $\alpha$ -HCH and 0.41 (0.19–0.56) for  $\gamma$ -HCH, in most cases suggesting a net volatilization for  $\alpha$ -HCH but equilibrium and/or net deposition for  $\gamma$ -HCH. Combined with the result that the average  $\alpha/\gamma$ -HCH ratio in soil ( $1.05 \pm 0.43$ ) was less than that in the technical mixture (5–14) and that in air ( $2.41 \pm 0.89$ ), it indicated that soil was an important sink for  $\gamma$ -HCH. The  $\gamma$ -HCH has a lower  $K_{aw}$  and higher  $K_{oa}$  than  $\alpha$ -HCH, and therefore more  $\gamma$ -HCH can reach to the soil through dry/wet deposition in addition to air–soil exchange, and the retention of  $\gamma$ -HCH in most soils might be increased (Li and Wania, 2005). The volatilization status of  $\alpha$ -HCH were caused by the high vapor pressures and low  $K_{oa}$  value of  $\alpha$ -HCH (Shoeib and Harner, 2002; Růžicková et al., 2008), but the temperature dependence of  $\alpha$ -HCH showed the influence of LRAT, indicating the contribution from soil volatilization to atmospheric  $\alpha$ -HCH was minor compared with LRAT. The average ratio of  $\alpha/\beta$ -HCH in soil ( $1.10 \pm 1.77$ ) was much lower than that in the atmosphere ( $6.23 \pm 4.06$ ), implying relatively high soil  $\beta$ -HCH concentrations (Table S3). Owing to the strongest resistance to degradation,  $\beta$ -HCH was relatively more concentrated in the soil than  $\alpha$ -HCH.

The average  $ff$  value for  $p,p'$ -DDT was 0.55 (0.16–0.81), showing equilibrium and/or volatilization status. In contrast, the average  $ff$  values for other DDT homologues were less than 0.5 (0.42 for  $o,p'$ -DDT, 0.26 for  $p,p'$ -DDE, etc.), suggesting deposition status. Significant relationships of  $p,p'$ -DDT concentrations in air and soil are shown in Fig. S5, which support the high temperature dependence of  $p,p'$ -DDT, implying contribution from air–soil volatilization

across the whole sampling campaign. Moreover, the average ratios of  $p,p'$ -DDT/ $o,p'$ -DDT and  $p,p'$ -DDT/ $p,p'$ -DDE in soil were both higher than those in air (Table 5), suggesting fresh technical  $p,p'$ -DDT input in the soil and indicating that the soil was a potential source of  $p,p'$ -DDT to air. Owing to the large use over the last few decades, there are still a large amount of residue  $p,p'$ -DDT in soil. The high temperature dependence but deposition status of  $p,p'$ -DDE indicated the influence of LRAT and that the soil at the sampling site was an important sink for atmospheric  $p,p'$ -DDE.

The  $ff$  values for chlordanes ranged from 0.25 to 0.96, and the average  $ff$  values were  $0.72 \pm 0.22$  for TC and  $0.72 \pm 0.18$  for CC, indicating volatilization of chlordanes (Fig. 8). The average TC/CC ratios were  $1.77 \pm 0.37$  in air and  $1.56 \pm 0.21$  in soil, which were both higher than that in technical chlordane (1.1–1.3), indicating fresh chlordane input to soil and air. Temperature dependence and air concentrations of TC and CC suggested that except for the volatilization from soil, the atmospheric chlordane at JSH was also strongly affected by the LRAT and the ongoing sources (such as chlordane and heptachlor). These results suggested the fresh input of chlordanes in regional environment. Wang et al. stated that the total usage before adjustment from 1988 to 2008 was 2745 t, accounting for approximately 80% of the production in the same period, which was widely used in fighting termites to protect new constructions in central and south China (Wang et al., 2013).

The fugacity fraction values varied widely for endosulfans (0.07–0.98) (Table S5), implying the equilibrium for  $\alpha$ -endosulfan (Fig. 8) and equilibrium and/or volatilization for  $\beta$ -endosulfan (Table S5). This was in accordance with the finding that the average  $\alpha/\beta$ -endosulfan ratio in soil ( $0.32 \pm 0.18$ ) was less than that in air ( $1.09 \pm 0.58$ ). The relatively low  $\alpha/\beta$ -endosulfan ratios in soil were related to the higher  $\beta$ -endosulfan concentrations in soil, which was likely to be due to the lower degradation rate of  $\beta$ -endosulfan in soil. Overall, endosulfans can reside for a longer time in soil than in air. This was consistent with those results of the high temperature dependence of endosulfans and the status of soil–air exchange, suggesting the primary influence of soil volatilization on atmospheric endosulfan.

The  $ff$  values for HCB ranged from 0.58 to 0.98, which were relatively high compared with other OCPs (Table S5), indicating a net volatilization from soil to air. The relatively high  $ff$  values were related to the relatively high soil concentrations (Table S3) and low  $K_{oa}$  value ( $10^{7.38}$ ) (Shoeib and Harner, 2002). A strong negative correlation between air concentrations and  $ff$  values of HCB ( $R^2 = 0.788$ ,  $p < 0.01$ , 2-tailed) was measured (Fig. S5), indicating the increased air concentrations were accompanied by reduce  $ff$  values. Thus, the decreased  $ff$  values in winter (Table S5) were attributed to the increased air concentrations, indicating that the combustion of heating fuels in the surrounding areas was an important source of atmospheric HCB (see Section 3.2).

PCBs showed a declining trend in  $ff$  values from lower chlorinated PCBs to higher chlorinated PCBs (Fig. 8), with mean values were 0.56 (0.27–0.92) for PCB 28, 0.50 (0.26–0.90) for PCB 52, 0.26 (0.11–0.55) for PCB 101 and 0.12 (0.03–0.34) for PCB 118, respectively. This indicated equilibrium and/or net volatilization for lower chlorinated PCBs and net deposition for higher chlorinated PCBs. This pattern was almost the same as that in Chinese background sites (Zhang et al., 2008). Temperature dependence of PCBs

**Table 5**  
Average air and soil ratios for selected OCPs.

Mean $\pm$ std. (ng/g)	$\alpha/\beta$ -HCH	$\alpha/\gamma$ -HCH	$o,p'$ -DDT/ $p,p'$ -DDT	$p,p'$ -DDT/ $p,p'$ -DDE	TC/CC	$\alpha/\beta$ -endosulfan
Air	$6.23 \pm 4.06$	$2.41 \pm 0.89$	$0.97 \pm 0.15$	$0.45 \pm 0.24$	$1.77 \pm 0.37$	$1.09 \pm 0.58$
Soil	$1.10 \pm 1.77$	$1.05 \pm 0.43$	$0.24 \pm 0.05$	$2.52 \pm 1.42$	$1.56 \pm 0.21$	$0.32 \pm 0.18$

suggested the influence of LRAT, and the foreign PCBs elevated the air levels at JSH and led to equilibrium and/or deposition between air and soil. In addition, volatilizations of lower chlorinated PCBs from soil to air had a partial impact on air concentrations. The lower chlorinated PCBs have faster volatilization rates and are more active during the air–soil transfer process, whereas the higher chlorinated PCBs show greater retention in the soil compared with lower chlorinated PCBs (Syed et al., 2013a). Significant negative correlations between *ff* values and air concentrations were observed (Fig. S5), especially for PCB 28 ( $R^2 = 0.795$ ,  $p < 0.01$ ) and PCB 52 ( $R^2 = 0.663$ ,  $p < 0.01$ ), indicating the impact of LRAT. Overall, the lower chlorinated PCBs in the atmosphere were primarily influenced by LRAT and followed by soil–air volatilization, whereas higher chlorinated PCBs were mainly affected by LRAT. Owing to the strong adsorption of their particulate phase and low volatility of their gas phase, deposition of higher chlorinated PCBs were observed during the sampling period, and therefore the soil at the study area was an important sink for higher chlorinated PCBs.

#### 4. Conclusion

In this study, air and soil concentrations, seasonal variations, and air–soil exchanges for atmospheric OCPs and PCBs at JSH were investigated. The concentrations of OCPs in the atmosphere were comparable to or lower than those of other background/rural sites, whereas the concentrations in soil were relatively low. The concentrations of PCBs both in soil and air were lower than those of other remote areas. Significant seasonal variations of most OCPs and PCBs in the atmosphere were observed during the sampling period, with relatively high concentrations in summer and low concentrations in winter, whereas HCB showed an opposite seasonal variation. Higher concentrations of HCB compared with other compounds in air and negative temperature dependence suggested the surrounding ongoing source (e.g. HCB emissions from fuel consuming activities, especially in the wintertime). The ratios of contaminants in air and soil indicated the recent input of *p,p'*-DDT in soil and fresh input of chlordane both in air and soil. Temperature dependence and fugacity fraction (*ff*) values indicated that the soil was an important source for most OCPs and PCBs, especially for *p,p'*-DDT and endosulfan, suggesting the re-volatilization of residual compounds in the soil was the main influencing factor on their atmospheric concentrations. For HCHs and other PCB compounds, weak temperature dependences implied the main influence of LRAT, which was well matched with the characteristics as a background site. The exchange directions between soil and air were largely connected with the volatility of compounds, e.g. HCHs were mostly volatilized from soil to air, while the degradation products of DDT were mainly deposited in soil; and lower chlorinated PCBs were typically volatilized but higher chlorinated PCBs were deposited.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2017.08.003>.

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